

952256

68-

N.F.

NCL 68-45R

EFFECTS OF IMPURITIES ON CARRIER LIFETIME
IN BULK SOLAR-CELL MATERIAL

QUARTERLY REPORT

AUGUST 1968

Letter Contract No. 952256

N 68-33104

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
	19	1
	(PAGES)	(CODE)
	CR-96272	26
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

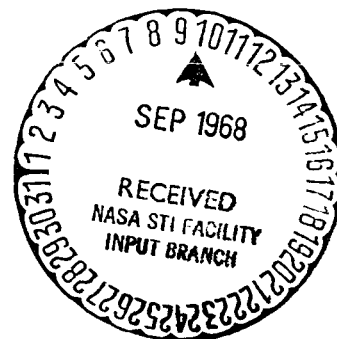
NORTHROP CORPORATE LABORATORIES
3401 West Broadway
Hawthorne, California 90250

GPO PRICE \$ _____

CSFTI PRICE(S) \$ _____

Hard copy (HC) 3.00

Microfiche (MF) .65



NCL 68-45R

EFFECTS OF IMPURITIES ON CARRIER LIFETIME
IN BULK SOLAR-CELL MATERIAL

QUARTERLY REPORT

AUGUST 1968

Letter Contract No. 952256

This work was performed for the
Jet Propulsion Laboratory, California
Institute of Technology, as sponsored
by the National Aeronautics and Space
Administration under Contract NAS 7-100

NORTHROP CORPORATE LABORATORIES
3401 West Broadway
Hawthorne, California 90250

PRECEDING PAGE BLANK NOT FILMED.

NOTICE

This report contains information prepared by Northrop Corporate Laboratories under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration

NEW TECHNOLOGY

All technological development to date are reported herein. They are considered to be unreportable under the instructions of NHB 2170.2 dated October 1966.

ABSTRACT

Information has been gathered regarding the feasibility of employing certain impurities as dopants in silicon. On the basis of this information the effects of Li, Na, Be, Cl and Al as dopants and very high oxygen concentrations in both n- and p-type material will be investigated. Crystals containing each of these impurities except Li are being prepared. The diffusion of Li into relatively thick slabs of crucible-grown Si containing As or P has been investigated. These experiments have demonstrated an apparent loss of Li from the surface during heating in vacuum. Isochronal annealing studies have been performed on samples following Co⁶⁰ gamma irradiation. The results indicate that the annealing behavior is dose dependent.

CONTENTS

	Page No.
INTRODUCTION	1
TECHNICAL DISCUSSION	2
Properties of Potential Dopant Impurities	2
More Conventional Impurities	5
Lithium Diffusion Studies	6
Dose Dependence of Lifetime Annealing in Co ⁶⁰ Gamma-Irradiated Silicon	10
Radiation Effects in Aluminum-Doped Silicon	12
Conclusions and Future Plans	13
REFERENCES	14

INTRODUCTION

The degradation and subsequent thermal recovery of the electrical properties of bulk semiconductor materials following exposure to various types of radiation have been shown to depend upon the type and concentration of impurities present. In Si containing the more commonly used dopants (As, Sb, and P in n-type and B and Ga in p-type), the radiation response is, for the most part, determined by the oxygen concentration although dopant effects are also observed, particularly upon annealing. On the other hand, Si diodes and solar cells containing Li have been shown to be more radiation resistant and to anneal faster than similar devices which do not contain this impurity.

Because of these observed impurity effects and the need to produce devices capable of operating in a radiation environment, it is natural to inquire whether the use of other less common dopant impurities might not provide even greater benefits. One purpose of this research is to evaluate the possibilities of employing certain impurities as dopants and to investigate the degradation of the carrier lifetime by radiation in material containing those dopants which can be incorporated in the Si lattice without degrading the lifetime.

We have observed that small amounts of electron- (or gamma) induced damage anneals more readily than larger doses. This dose dependence and the annealing kinetics are being investigated with the practical viewpoint that damage in space systems might be eliminated by annealing at reasonable temperatures.

Bulk properties of Li-doped Si are poorly understood. The efforts undertaken in this program with Li-doped material are intended to help separate bulk properties and device effects in the observations made on Li-doped solar cells.

TECHNICAL DISCUSSION

PROPERTIES OF POTENTIAL DOPANT IMPURITIES

A literature survey was conducted to obtain information regarding the practicality of using certain impurities as dopants in Si. Factors which were especially considered were the solid solubility and diffusibility of the impurities in Si and the possible action of such impurities as recombination centers. Knowledge of the first two properties is necessary to determine whether the impurity can be incorporated in Si and, if so, the proper method of doing so, i. e., by diffusion or by adding to the melt. It is, of course, desirable to know something about the possible recombination properties of the impurity to avoid degrading the lifetime.

Much of this information was provided by the Electronic Properties Information Center (EPIC). Additional information was obtained from a survey of Chemical Abstracts from 1945 to the present. The results of these surveys are summarized below.

Lithium. The diffusion properties of Li are expressed through the relationship¹

$$D = 2.65 \times 10^{-3} \exp (-14.5/RT)$$

In practice Li will diffuse ~ 1 mm/hr at 425°C. Since Li introduces levels only² at $E_c - 0.03$ eV, no appreciable effect on recombination is observed. The maximum solid solubility³ is $\approx 2 \times 10^{18}$ cm⁻³ at 500°C. Its distribution coefficient is⁴ 0.01.

Sodium. There is considerable controversy on the diffusion of Na into Si. McCaldin and Widmer^{5, 6} concluded that after 180 hr at 800°C in Na vapor, no detectable concentration of Na was present except near the surface. On the other hand, using direct diffusion of Na from molten metal, Svob⁷ obtained

$$D = 1.65 \times 10^3 \exp (-16.7/RT).$$

Dr. Charles Fuller pointed out⁸ that it would be very difficult to avoid the effects of Li impurities in such an experiment, and, indeed, the similarity of the results to that for Li may be significant. In regard to possible action as recombination centers, Svob reported that no deep levels were present. Therefore, if his results are valid, one would expect no recombination difficulties. Again, if Svob's data are correct, the solid solubility is $\approx 10^{18} \text{ cm}^{-3}$ at 600°C, and the atoms enter interstitially. McCaldin, Little and Widmer⁶ indicate that Na tends to become substitutional after entering the lattice interstitially.

Potassium. Again, Svob reported data about diffusion of K. The data given should be considered in light of the above discussion. Diffusibility in Si is given by

$$D = 1.1 \times 10^{-3} \exp (-17.5/RT).$$

As for Na, no recombination is expected. The solid solubility is $\approx 8 \times 10^{17} \text{ cm}^{-3}$ at 600°C, and the atoms are introduced interstitially.

Beryllium. We have not located data on Be, but Trumbore³ discusses correlations between distribution coefficient and tetrahedral radius for elements in various columns of the periodic table. The tetrahedral radius for Be is⁹ 1.06Å. The distribution coefficient is estimated to be $10^{-3} \geq 10^{-4}$. The diffusion characteristics are unknown. However, it appears unlikely that it would be a particularly easy element to diffuse, and the estimated solid solubility at temperatures much below the Si melting point is fairly low. In regards to possible effect on recombination, although data have not been located for Be, it is natural to make comparison with Mg and Zn, both of which show deep levels: Mg at¹⁰ $E_c - 0.25 \text{ eV}$ ¹ and Zn with levels^{11, 12} at $E_c - 0.55 \text{ eV}$ and $E_v + \approx 0.32$.

It seems likely that one or more deep levels exist for Be, but since they appear shallower for Mg than Zn, they may not be a problem. Maximum solid solubility can be estimated⁴ from the distribution coefficient. The result is $\sim 10^{18}/\text{cm}^3$. By introduction into the melt, a concentration of $\sim 10^{17}/\text{cm}^3$ should be practical. Amounts obtainable by diffusion would be lower. The method of entrance into the lattice is unknown. However, Zn is presumably substitutional, and the above estimates are based on Be entering in the same fashion.

Magnesium. Being in the Be-Mg-Zn sequence, much that was said above is pertinent to Mg. However, some of the discussion of the recent conference on Si (Li) held at Goddard seems pertinent. D. Kendall (Texas Instruments), J. A. Baicker (Princeton Research), and P. H. Fang (Goddard) mentioned failures in attempts to dope with Mg. J. R. Carter (TRW) however, reported that Semi Elements had grown a p-type crystal containing 2.7 ppm Mg. The diffusion properties are unknown.¹³

Low lifetime might exist in material containing Mg, since a level at¹⁰ $E_c - 0.25 \text{ eV}$ is unfavorable. Since its tetrahedral radius is larger than for Zn (1.40\AA vs 1.31\AA), its distribution coefficient should be lower, $10^{-5} > K \geq 10^{-6}$, yielding a maximum solid solubility of $\sim 10^{16} \text{ cm}^{-3}$, about 0.1 that for Be.

Calcium. As just discussed, Be and Mg have properties which make their introduction into Si difficult, at least. The large radius of Ca, $\sim 1.7\text{\AA}$, makes it very unlikely that any measurable quantities can be introduced into Si. This is especially true since, as Trumbore³ points out, there is a critical radius where distribution coefficient drops very rapidly, and for Si this is $\sim 1.5\text{\AA}$. Crude guesses for parameters might be: distribution coefficient $\sim 10^{-8}$ and maximum solid solubility $\sim 10^{-4} \text{ cm}^{-3}$. Further, by analogy to Mg and Zn, it appears likely that any centers might be effective for recombination.

Sulfur. Sulfur is interesting as a possible impurity because it lies directly under O in the periodic table. As is well known and will be discussed briefly later, O has beneficial effects when present in quantities of $\sim 10^{17} \text{ cm}^{-3}$. However, S has a covalent radius of 1.04 \AA , as compared to 0.66 \AA for O, which makes its introduction more difficult. Its diffusion relationship is¹⁴

$$D = 0.92 \exp (-51/RT).$$

Sulfur introduces a number¹⁵ of deep levels into Si ($E_c - 0.11, 0.19, 0.37$ and 0.61 eV) and thus is probably a good recombination center. Its solid solubility is³ $\sim 10^{16} \text{ cm}^{-3}$ at 1200°C . So, although its similarity to oxygen would seem to give large potential as a useful dopant, sulfur is difficult to diffuse, has a fairly low solid solubility and introduces prospective recombination levels. Therefore, it seems a poor choice for a dopant.

Fluorine, Chlorine, Bromine. There is a dearth of information on doping with F, Cl, and Br. One would guess, on the basis of the discussion of Trumbore³ and their tetrahedral radii ($0.64, 0.99$ and 1.11 \AA , respectively), that introduction would be feasible either by diffusion or by introducing into the melt. The recombination behavior might very well depend on whether introduced atoms were substitutional or interstitial, which is also unknown.

MORE CONVENTIONAL IMPURITIES

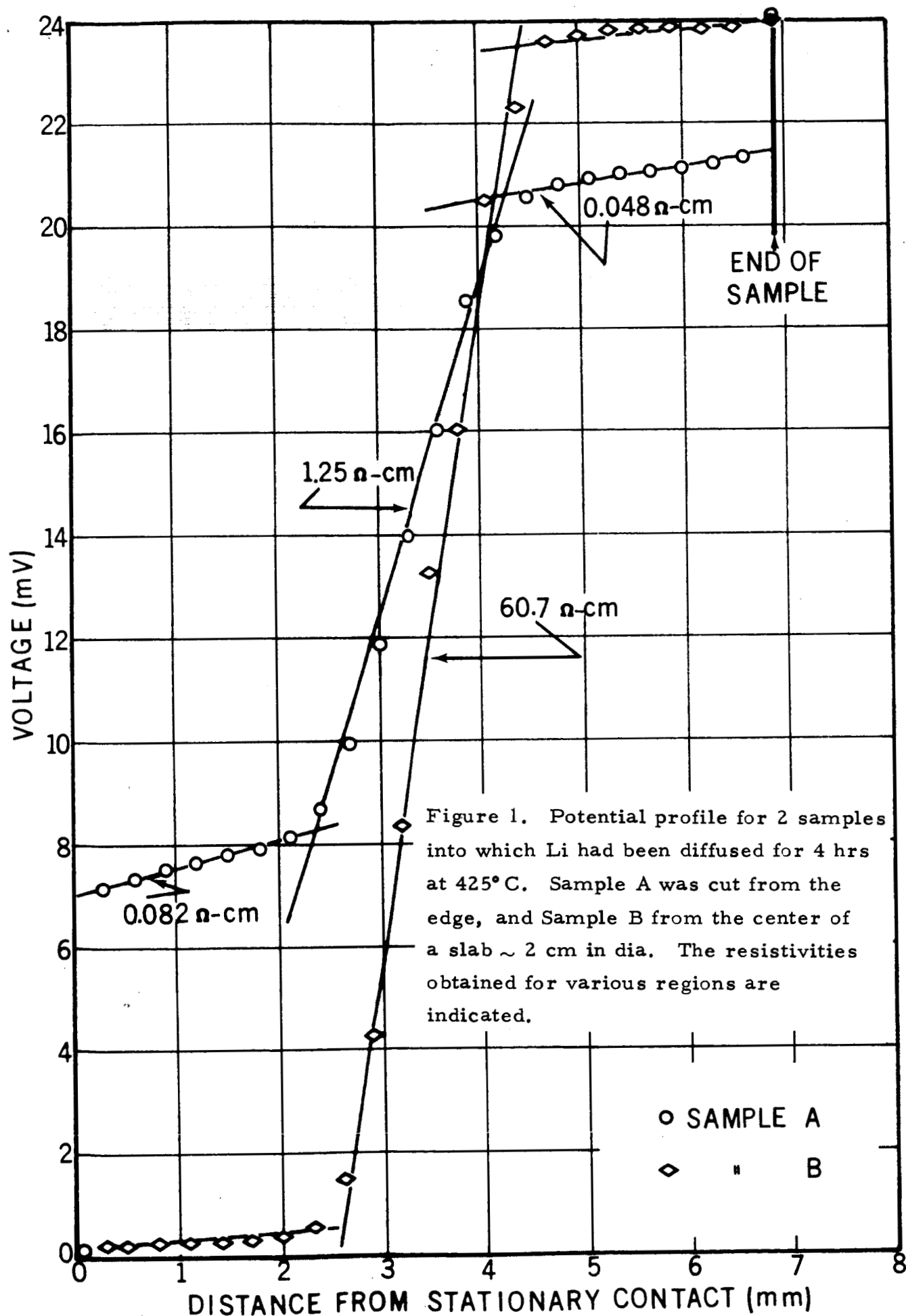
Oxygen. It has been known for some time¹⁶ that O-containing Si suffers less lifetime degradation under some circumstances than material with much lower O concentration. Recent studies at Northrop Corporate Laboratories have confirmed this fact for n-type material irradiated with 10-MeV electrons, and it has been observed that O assists dramatically in recovery of damage in p-type Si. The maximum solid solubility of O in Si is³ $2 \times 10^{18} \text{ cm}^{-3}$, about a factor of 20 higher than is normally observed. It would not seem unreasonable to strive for a concentration near the maximum value. The question is, "If some helps, would more be better?"

Aluminum. Work performed ¹⁷ at Northrop Corporate Laboratories strongly indicates that Al-doped Si undergoes smaller changes in lifetime when exposed to neutron irradiation than material doped with B or Ga. Some uncertainty in the data exists because of the poor quality of the Al-doped material, but since Al is a reasonably common dopant, good material should be obtainable. It seems clear that if such an effect occurs for neutron irradiation it would be observed under low-energy electron irradiation.

On the basis of the above information, it was concluded that the addition of Na, Be, and O to n-type material and of Al, Cl and O to p-type would perhaps be feasible. Various crystal manufacturers were requested to submit bids for supplying to- to 100-gram ingots containing each of these impurities and an order was placed with Semi Elements, Inc., for six such crystals. These materials are scheduled for delivery in late August. In addition to these ingots, a large Al-doped crystal grown in argon by the float-zone process was obtained from the General Electric Company and a similar crystal has been ordered from Texas Instruments, Inc., for comparison.

LITHIUM DIFFUSION STUDIES

A series of experiments was performed to determine whether Li can be uniformly distributed in large bulk Si lifetime samples by the proper diffusion technique. For these studies, pure Li was vacuum evaporated on opposite sides of 50 to 60 Ω cm silicon slabs from 3 to 7 mm thick which were heated in vacuum for four hours at 425°C to diffuse the Li. The slabs were then removed from the vacuum, etched to remove the excess Li, and were reheated in vacuum at temperatures from 425° to 450°C for periods of from 8 to 66 hours in order to redistribute the Li. Following this treatment, the slabs were re-etched and small bars cut from them. Electrical contacts were applied to the surfaces upon which the Li had been evaporated, and a potential profile was obtained for each sample by



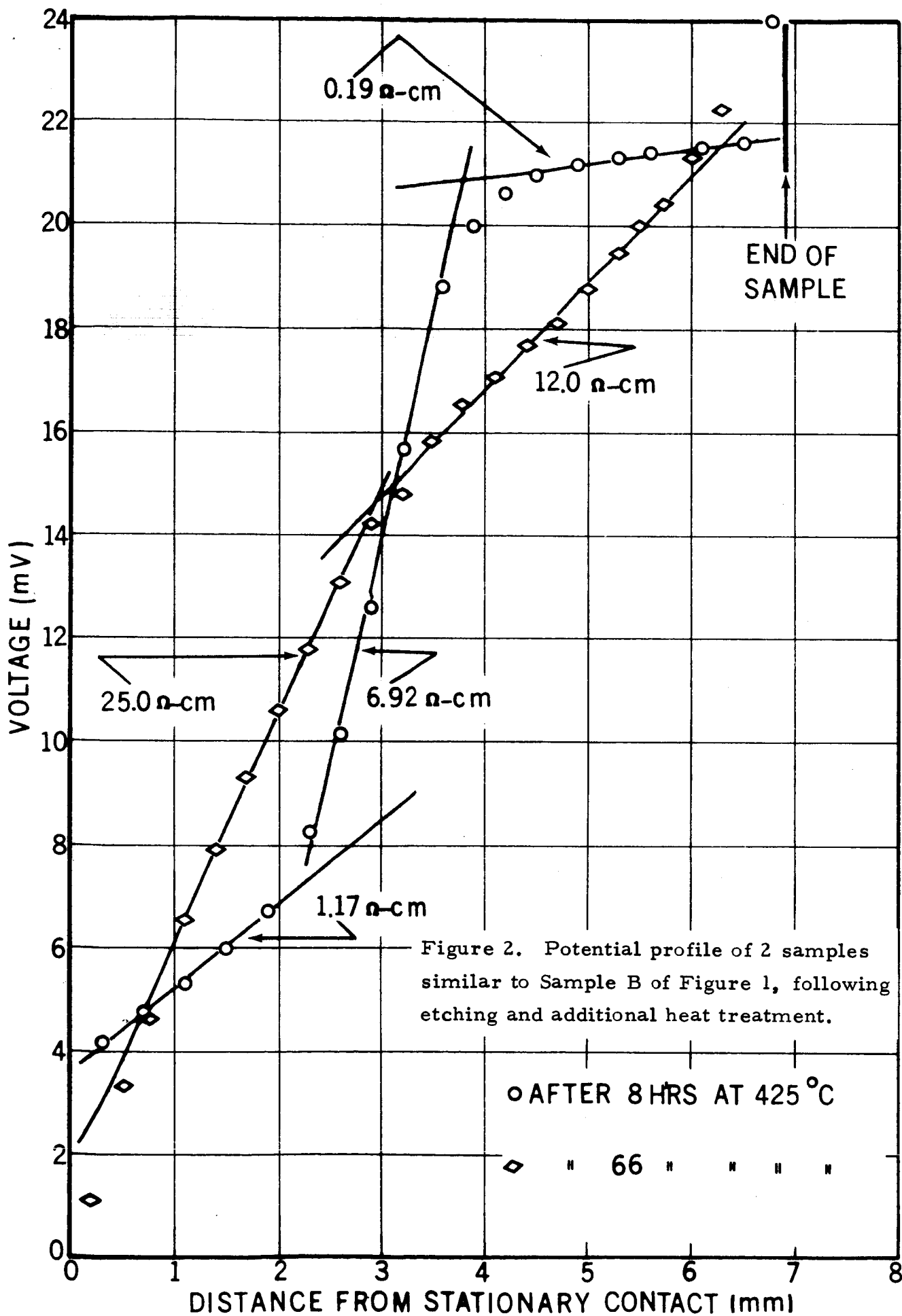


Figure 2. Potential profile of 2 samples similar to Sample B of Figure 1, following etching and additional heat treatment.

measuring the voltage as a function of position along the bar while a constant current was passed through it. The slope of the potential-vs-length curve yielded the resistivity and variations in the Li concentration were manifested by deviations of the curve from a straight line.

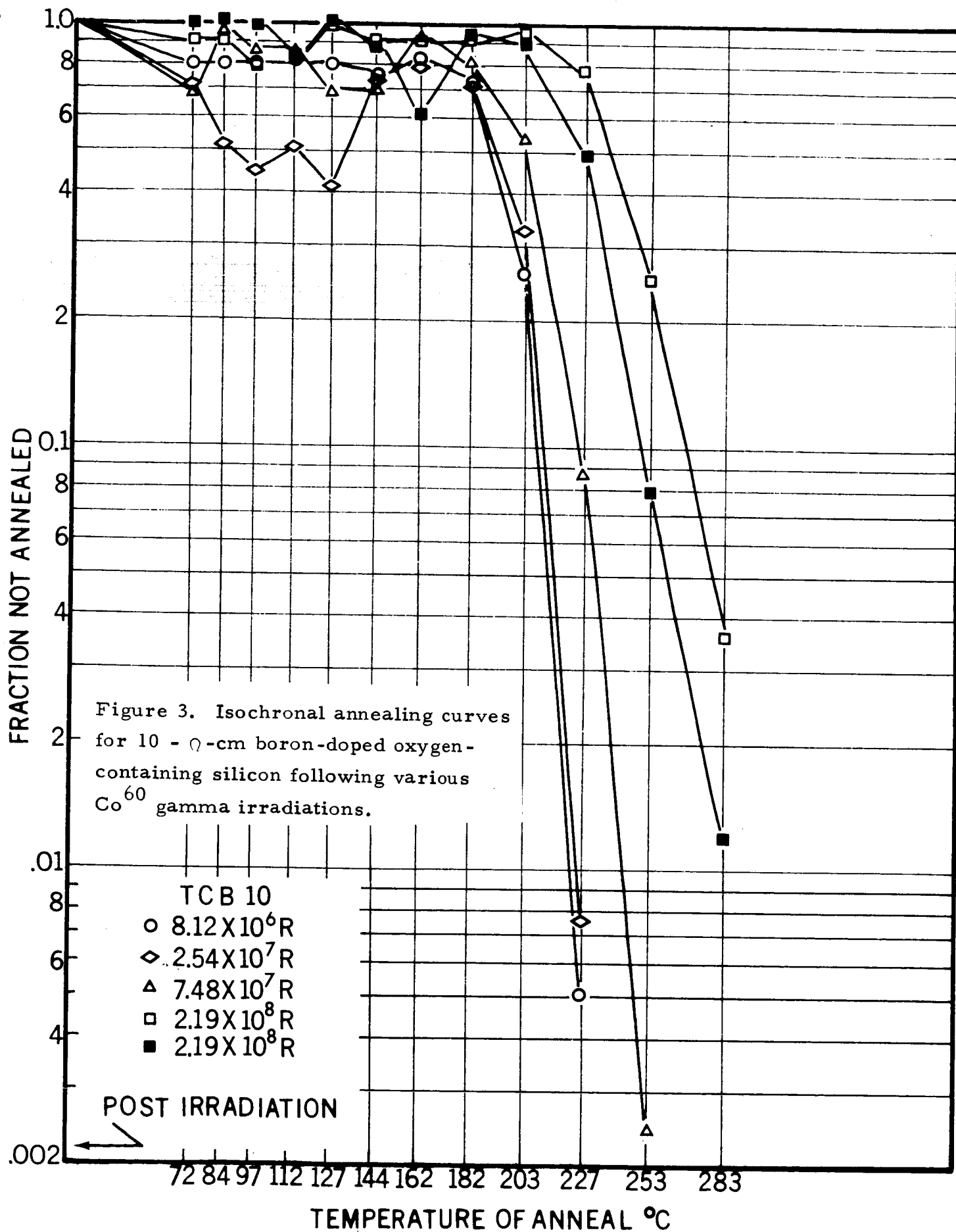
Profiles obtained for samples after various treatments are shown in Figures 1 and 2. Figure 1 shows results for two samples which were cut from a slab of 60 Ω cm material into which Li had been diffused for four hours at 425° C but before any attempts had been made to distribute the Li. The resistivity of each sample is indicated at various regions along the length. The results indicate that most of the Li was relatively evenly distributed in the outer 2-4 mm of each sample during the diffusion process and that essentially none reached the interior of sample B. This sample was cut from the middle of the slab and thus had no surfaces common to the slab other than the ends. Sample A, on the other hand, contained three surfaces common to the original slab and the low resistivity of the interior region was due to diffusion from the third surface.

Relatively large samples ($\sim 7 \times 7 \times 30$ mm) are normally used for lifetime studies to minimize surface effects, and the results of Figure 1 indicated that additional heat treatment would be required to distribute Li evenly throughout samples of this thickness. Figure 2 shows the results of heating a 60 Ω cm sample for different periods at 425° C after Li had been diffused for 4 hrs at that temperature. As indicated by the curves, three distinct regions have different resistivities were apparent after heating for 18 hrs at 425° C. The resistivity of the central portion of the sample was reduced to ~ 7 Ω cm by diffusion from the ends while the end regions were increased in resistivity due to the loss of Li. The fact that the ends were not the same resistivity was probably due to differences in the initial concentration of Li on the surfaces. After the sample was heated an additional 48 hrs at 425° C, it exhibited only two regions of more or less uniform resistivity. However, the resistivity of both regions was higher than the central portion before this treatment, indicating Li was either precipitating

or being lost from the surfaces. Additional experiments were conducted in which samples were given various heat treatments after being diffused for 4 hrs at 425°C before the excess Li was etched from the surface. The results of these experiments were similar to those shown in Figure 2; that is, samples heated less than ~ 24 hrs at 425 to 450°C exhibited three regions of different resistivity, while those which were heated for 40 to 66 hrs at these temperatures exhibited only two regions. The resistivity of these regions increased as both the temperature and the heating time were increased. Because of this apparent loss of Li from the surface before uniform distribution is achieved, it may be necessary to perform the heat treatments in an inert atmosphere. The apparatus which was used for these experiments is currently being modified to provide such an atmosphere. When this modification is completed, attempts will be made to distribute Li in both He and N₂ atmospheres.

DOSE DEPENDENCE OF LIFETIME ANNEALING IN Co⁶⁰ GAMMA-IRRADIATED SILICON

Five lifetime samples measuring ~ 7 x 7 x 30 mm were cut from the same Si crystal and were exposed at dry ice temperatures (-78°C) to different damage levels in the Northrop Co⁶⁰ gamma source. The samples were isochronally annealed for 30 min at 11 different temperatures between 72°C ($10^3/T^{\circ}\text{K} = 2.9$) and 283°C ($10^3/T^{\circ}\text{K} = 1.8$) to determine whether the recovery of the lifetime damage produced by this type of radiation is dependent upon the dose. Such dose dependent annealing behavior is observed in Si solar cells irradiated with 4.6-MeV protons¹⁸ and in bulk Si irradiated with 10-MeV electrons¹⁹. The results of these annealing experiments are shown in Figure 3 which shows the fractional change in the reciprocal lifetime (measured at 30°C) remaining after anneals at the indicated temperatures. Since the recombination center concentration is expected to vary inversely with the lifetime, the curves indicate the fraction of radiation-induced recombination centers remaining after each



anneal. The fraction not annealed, f , is defined by

$$f \equiv \frac{\frac{1}{\tau_t} - \frac{1}{\tau_o}}{\frac{1}{\tau_\phi} - \frac{1}{\tau_o}}$$

where τ_t is the lifetime at 30°C following an anneal at temperature T , and τ_o and τ_ϕ are the lifetimes at 30°C before and after irradiation, respectively. The annealing temperatures represent equal intervals on a $1000/T^\circ\text{K}$ scale but are shown in degrees centigrade for convenience.

As illustrated in the figure, all of the samples exhibited large recovery at high temperature but the temperature required to produce essentially complete anneal increases with increasing dose. Less than 1% of the damage remained in samples 1 and 2 after the anneal at 227°C while sample 3 dropped below this value following anneal at 253°C. Samples 4 and 5 were annealed at 315°C although the amount of recovery has not been determined at present.

As indicated in the figure, samples 4 and 5 were exposed to the same dose but display somewhat different rates of recovery at high temperature. The relatively faster recovery exhibited by sample 5 may be related to a relatively small damage rate exhibited by this sample during the earlier period of irradiation. Other details of the annealing curves differ among samples demonstrating the complexity of the process.

These five samples will be reirradiated using a relatively light dose and the anneals will be repeated to determine whether the annealing behavior is still dependent upon the total dose.

RADIATION EFFECTS IN ALUMINUM-DOPED SILICON

Six lifetime samples were prepared from the Al-doped, float-zone crystal supplied by the General Electric Company. The lifetime of this material

is from 250 to 300 μ s which is much higher than that of the crucible-grown crystals containing this dopant and prepared by Texas Instruments which we have used previously. The lifetime measurements were complicated by the presence of a relatively large amount of trapping but the samples should prove satisfactory. Two of the samples will be used to study 2-MeV electron damage.

CONCLUSIONS AND FUTURE PLANS

On the basis of information obtained regarding the metallurgical properties of various impurities in Si and of the possible role of such impurities as recombination centers, it was concluded that a study of n-type material containing Na, Be, and O and of p-type material containing Al, Cl, and O would be of interest. Crystals containing these impurities are being prepared.

Attempts to distribute Li uniformly throughout slabs of Si having dimensions similar to those of lifetime samples have been only partially successful. The apparent loss of Li from the surface after prolonged heating in vacuum suggests that the heat treatments should be performed in an inert atmosphere.

Annealing experiments performed on samples exposed to different Co^{60} gamma doses indicate the rate of recovery at high temperature is dose dependent. These experiments will be continued to determine whether the annealing behavior is dependent upon the total dose and whether such behavior is reproducible.

Measurements of samples made from Al-doped, float zone material indicate that the lifetime of this material is much longer than that of similar material grown by the Czochralski (quartz crucible) process. The samples should consequently provide a valid comparison between the response of Al- and B-doped material to 2-MeV electron damage.

REFERENCES

1. B. Pratt and F. Friedman, "Diffusion of Lithium into Ge and Si," J. Appl. Phys. 37, 1893-1896 (1966)
2. Aggarwal, R. L. et al., "Excitation Spectra of Lithium Donors in Silicon and Germanium," Phys. Rev., v. 138, No. 3A, May 3, 1965, p. A882-893.
3. F. A. Trumbore, "Solid Solubilities of Impurity Elements in Germanium and Silicon," Bell Sys. Tech. J., 39, 205-234 (1960).
4. Schibli, E. and A. G. Milnes, "Deep Impurities in Silicon," Matl. Sci. and Eng., v. 2, no. 4, Nov. 1967, p. 173-180.
5. J. O. McCaldin and A. E. Widmer, Proc. IEEE 52, 301 (1964).
6. J. O. McCaldin, M. J. Little and A. E. Widmer, "The Solubility of Sodium in Silicon," J. Phys. Chem. Solids, 26, 11-29 (1965).
7. L. Svob, Solid State Electronics 10, 991-996 (1967).
8. Personnel communication.
9. Pauling, Linus The Nature of the Chemical Bond, Chap. 2, Cornell Univ. Press (1960).
10. Franks, R. K. and J. B. Robertson, "Magnesium as a Donor Impurity in Silicon," Solid State Comm., v. 5, no. 6, June 1967, p. 479-481.
11. Carlson, R. O., "Double-Acceptor Behavior of Zinc in Silicon," Phys. Rev., V. 108, no. 6, Dec. 15, 1957, p. 1390-1393.
12. Kornilov, B. V., "Absorption in Silicon Doped with Zinc," Sov. Phys. Solid State, v. 5, no. 11, May 1964, p. 2420-2424.

REFERENCES (continued)

13. These comments are based on personal recollections. This discussion will presumably be published soon as part of the conference proceedings.
14. Carlson, R. O., R. N. Hall and E. M. Pell, "Sulfur in Silicon," Phys. & Chem. of Solids, v. 8, Jan. 1959, p. 81-83.
15. Krag, W. E., et al, "Sulfur Donors in Silicon Infrared Transistions and Effects of Calibrated Uxi axial Stress, "Phys. of Semiconductors Proc. of the International Conference, Kyoto, 1966, published by the Phys. Soc. of Japan, Tokyo, 1966, p. 230-233.
16. Inuishi, Y. and Matsuura, K. Phys. Soc. Japan.
17. Curtis, Bass and Germano, Rpt. 235-3 for Harry Diamond Labs.
18. Faraday, B. J., R. J. Statler, and R. V. Tauke "Thermal Annealing of Proton-Irradiated Silicon Solar Cells", Proc. IEEE 56, 31 (1968).
19. Bass, R. F. and O. L. Curtis, Jr., "Annealing of 10 MeV Electron Damage in Silicon", to be published.